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| (54) Title: AMPHOTERIC POLYACRYLAMIDES AS DRY STRENGTH ADDITIVES FOR PAPER (57) Abstract This invention relates to a process for making paper comprising: a) providing an aqueous pulp slurry; b) adding to the aqueous pulp slurry cationic polymer selected from the group consisting of cationic starch and cationic wet strength resin, and water-soluble amphoteric polymer made from monomers comprising: i) nonionic monomer selected from the group consisting of acrylamide and methacrylamide; ii) anionic monomer; and iii) cationic monomer, wherein the amount of anionic monomer plus cationic monomer is less than 9 mole percent of the total of anionic, cationic and nonionic monomer in the amphoteric polymer. The invention also relates to paper with improved dry strength made by said process. | | |

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AMPHOTERIC POLYACRYLAMIDES AS DRY STRENGTH ADDITIVES FOR PAPER

Field of the Invention

This invention relates to a process for making paper, which paper has improved dry strength.

Background of the Invention

5 It is well known in the art that the strength of paper can be increased by incorporating increased amounts of paper pulp into the product. However, this method of increasing strength substantially increases both the basis weight and the cost of the paper. A preferred method of increasing the strength is addition of small amounts of chemical additives that do not substantially increase the cost
10 or the basis weight of the product.

U.S. Patent No. 2,884,058 discloses improving the dry strength (tensile) of paper utilizing an amphoteric acrylamide polymer wherein the cationic groups are supplied by quaternary ammonium groups. The monomers used to supply the quaternary ammonium groups do not include
15 methacroyloxyethyltrimethylammonium chloride (MTMAC),
acroyloxyethyltrimethylammonium chloride (ATMAC),
methacroyloxyethylbenzyltrimethylammonium chloride (MBMAC),
dimethylaminoethylmethacrylate (DMAEMA) and salts of DMAEMA.,

U.S. Patent No. 5,032,226 discloses a base paper for photographic layer
20 carriers containing cationic wet strength resin and an amphoteric poly(meth)acrylamide for structural strength. It is stated that the molar ratio of the amide components to the sum of the anionic and cationic groups is preferably

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in the region of from about 60:40 to 95:5 in the amphoteric polymer, and that the ratio of the number of cationic groups to the number of anionic groups is between 10:1 and 1:2. In the examples the molar ratio of anionic monomer plus cationic monomer to uncharged monomer is 9:91 or greater.

5 U.S. Patent No. 5,391,225 discloses an alkenylsuccinic acid emulsion sizing agent wherein the emulsifying dispersant is an amphoteric acrylamide polymer containing from 0.1 to 20 mole % cationic monomer, from 0.1 to 20 mole % anionic monomer and from 50 to 99.8 mole % acrylamide or methacrylamide.

10 European Patent Application No. 0 580 529A discloses the use in paper of a predominantly cationic polyelectrolyte obtained from acrylamide, at least one anionic monomer at the 5-15 mole % level, and at least one cationic monomer at the 10-50 mole % level.

Japanese Patent Application No. 57047998(82)-A discloses that the
15 strength of paper can be improved by using an amphoteric polyacrylamide copolymer, an anionic paper strength improver, and aluminum sulfate.

Japanese Patent Application No. 88063678(88)-B discloses that paper with high strength is obtained by addition of first, an amphoteric acrylamide polymer, second, Al_2O_3 , and third, an amphoteric acrylamide polymer. The acrylamide
20 polymers contain 1 to 20 mole % anionic groups and 1 to 30 mole % cationic groups.

Japanese Patent Application No. 63050597(88)-A teaches that a paper strength intensifier comprises (meth)acrylamide, cationic monomer, α,β -unsaturated mono- or dicarboxylic acid, and difunctional vinyl monomer as
25 constituent monomers. The cationic monomers disclosed are dimethylaminoethyl (meth)acrylate and diethylaminopropyl (meth)acrylamide.

Summary of the Invention

It is an object of the present invention to overcome the disadvantages in the above mentioned paper containing cationic wet strength resin and amphoteric (meth)acrylamide polymers by providing paper and a process for making paper
5 whereby the amphoteric polymer contains only low levels of anionic and cationic monomers. These low levels are an obvious industrial advantage over the increased expense of the higher levels utilized previously.

The present invention relates to a process for making paper comprising:

- 10 a) providing an aqueous pulp slurry;
b) adding to the aqueous pulp slurry cationic polymer selected from the group consisting of cationic starch and cationic wet strength resin, and water-soluble amphoteric polymer made from monomers comprising: i) nonionic monomer selected from the group consisting of acrylamide and methacrylamide;
15 ii) anionic monomer; and iii) cationic monomer,

wherein the amount of anionic monomer plus cationic monomer is less than 9 mole percent of the total of anionic, cationic and nonionic monomer in the amphoteric polymer.

In a preferred embodiment of the invention the amphoteric polymer is
20 made from monomers comprising: i) nonionic monomer selected from the group consisting of acrylamide and methacrylamide; ii) anionic monomer; iii) cationic monomer; and iv) crosslinking monomer comprising at least one water-soluble divinyl monomer.

In another embodiment the invention also relates to paper made by said
25 process and paper with improved dry strength made by said process.

Detailed Description of the Invention

The amphoteric polymers of the invention are made from nonionic monomer selected from the group consisting of acrylamide and methacrylamide, anionic monomer, and cationic monomer, wherein the amount of anionic monomer plus cationic monomer is less than 9 mole percent of the total of anionic, cationic and nonionic monomer in the amphoteric polymer. The preferred nonionic monomer is acrylamide.

Anionic monomers for use in the invention are preferably α,β -unsaturated carboxylic acids such as e.g., acrylic acid, methacrylic acid, itaconic acid and salts thereof. More preferred anionic monomers are acrylic acid and methacrylic acids, or salts thereof; and the most preferred anionic monomer is acrylic acid or salts thereof. The preferable salts are sodium salts.

Cationic monomers for use in the invention include unsaturated monomers containing amino groups or quaternary amino groups. When monomers containing amino groups are used, cationic sites are obtainable by forming salts of the amino groups with mineral acids. Preferred unsaturated cationic monomers include methacryloyloxyethyltrimethylammonium chloride (MTMAC), acryloyloxyethyltrimethylammonium chloride (ATMAC), methacryloyloxyethylbenzyltrimethylammonium chloride (MBMAC) and the hydrochloride salt of dimethylaminoethylmethacrylate (DMAEMA-HCl). The most preferred cationic monomer is MTMAC.

The amphoteric polymers for use in the invention will have an amount of anionic monomer plus cationic monomer that is less than 9 mole percent, preferably less than about 8 mole percent, and more preferably less than about 7 mole percent, of the total of anionic, cationic and nonionic monomers. The range of mole percent of anionic monomer plus cationic monomer will be from

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about 1 to 9, preferably from about 5 to 9, and more preferably from about 5 to about 8.

The relative ratio of anionic monomer to cationic monomer in the amphoteric polymers may vary over a wide range. Preferably the molar ratio of cationic monomer to anionic monomer will be from about 0.5:1 to about 2:1. More preferably the ratio will be from about 0.6:1 to about 1.5:1, and most preferably from about 0.7:1 to about 1:1.

A small amount of water soluble, divinyl monomer may also be incorporated to increase the molecular weight of the amphoteric polymer without crosslinking it so that it becomes insoluble. Suitable divinyl- monomers include N,N'-methylenebisacrylamide, ethyleneglycol dimethacrylate and ethyleneglycol diacrylate.

The amphoteric polymers may be prepared by the general procedures described in U.S. Patent No. 5,543,446 to Rodriguez. The procedures involve dissolving the monomers in water, adjusting the pH to 3.0-6.0, preferably 4.0-5.0, purging with nitrogen to remove oxygen, and adding a binary redox free-radical initiator to convert the monomers to polymer. The monomer concentration in water is preferably from 10-25 weight percent. Copper ions may be included to control the polymer molecular weight. Twenty-five to 35 parts cupric ion per million parts acrylamide monomer are typically included to control molecular weight depending upon the monomers used and the monomer concentration. Copper ion is generally added as copper sulfate. The redox initiator consists of a reactive pair which forms free radicals on reaction with each other. A particularly useful pair consists of potassium bromate and sodium metabisulfite. Other pairs will be apparent to those skilled in the art. Aqueous

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solutions of the redox initiator components are added continuously to the purged monomer solution to cause polymerization of the monomers to polymer.

The polymer solutions so formed have Brookfield viscosities of about 2,000-20,000 cps at polymer concentrations of about 15-20 weight percent.

5 The polymers are further characterized by having reduced specific viscosities of about 0.5-2.0 dl/g at 0.05% concentration in 2 molal sodium chloride solution.

The paper of the instant invention is prepared by any of the procedures well known in the art. The amount of amphoteric polymer used will be any amount which is effective to increase the dry strength of the paper. Preferably
10 the amount of polymer will be from about 0.05% to about 4% based on the dry weight of pulp. More preferably the amount of polymer will be from about 0.1% to about 3%, and most preferably from about 0.15% to about 2% based on the dry weight of pulp.

In preparing the paper of this invention the cationic polymer selected from
15 the group consisting of cationic starch or cationic wet strength resin is utilized in addition to amphoteric polymer. By the term "cationic wet strength resin" is meant cationic polymers which when used alone in paper impart significant wet strength to the paper.

Exemplary cationic wet strength resins for use in the invention are
20 polymeric amine/epihalohydrin resins, glyoxal-modified acrylamide copolymer resins, polyethyleneimines and polyvinylamines.

Polymeric amine/epihalohydrin resins are selected from the group consisting of polyaminoamide/epihalohydrin resins, polyalkylenepolyamine/epihalohydrin resins, aminopolymer/epihalohydrin
25 resins, and polyaminoamide ureylene/epihalohydrin resins. The preferred epihalohydrin is epichlorohydrin.

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Cationic glyoxal-modified acrylamide copolymer resins and their use in paper for wet strength are disclosed in U.S. Patent No. 3,556,932 to Coscia et al.

5 Polyaminoamide ureylene/epihalohydrin resins are disclosed in U.S. Patent No. 4,537,657 to Keim.

Polyalkylenepolyamine/epihalohydrin resins include resins made by reaction of epihalohydrin, preferably epichlorohydrin, with diethylenetriamine, triethylenetetramine, tetraethylenepentamine, bis(3-aminopropyl)amine, hexamethylenediamine or polyethyleneimine. Amino polymer/epihalohydrin
10 resins include resins made by reaction of epihalohydrin, preferably epichlorohydrin, with poly(diallylamine) or poly(methyldiallylamine). Polyalkylenepolyamine/epihalohydrin resins and amino polymer/epihalohydrin resins are discussed by H.H. Espy in "Wet-Strength Resins and Their Application," Tappi Press, 1994, pages 13-44.

15 The most preferred cationic wet strength resins for the practice of the invention are the polyaminoamide/epihalohydrin resins. These resins are produced by reacting a saturated aliphatic dicarboxylic acid containing two to ten carbon atoms, preferably adipic acid, with a polyalkylenepolyamine containing from two to four ethylene groups, two primary amine groups, and one to three
20 secondary amine groups, such as diethylenetriamine, triethylenetetramine and tetraethylenepentamine, preferably diethylenetriamine, to form a polyaminoamide having secondary amine groups that are then alkylated with epihalohydrin, preferably epichlorohydrin, to form tertiary aminochlorohydrin groups. These groups self-alkylate to form hydroxyazetidinium groups, which
25 are considered responsible for wet strength in paper. They are cationic in character. Polyaminoamides containing tertiary amines in the backbone are

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disclosed in U.S. Patent Nos. 4,487,884 and 4,515,657 to Maslanka. If tertiary amines are present in the polyaminoamide or polyamine backbone, quaternary epoxide groups are produced. The actual procedure for synthesizing these wet strength resins differs from product to product, but the objective, to generate aminopolyamide/epihalohydrin functionality, remains the same.

Kymene® wet strength resins are the preferred polyaminoamide/epihalohydrin resins. Some examples of polyaminoamide/epihalohydrin Kymene® wet strength resins, available from Hercules Incorporated, Wilmington, DE, are Kymene® 557H, Kymene® 557LX, Kymene® 557 SLX, Kymene® 557 ULX and Kymene® Plus. In Kymene® 557H adipic acid is reacted with diethylenetriamine to form a polyaminoamide that is alkylated and crosslinked with epichlorohydrin to form a polyaminoamide/epichlorohydrin resin. Kymene® Plus is a higher solids version of Kymene® 557H. Kymene® 557LX, Kymene® 557SLX and Kymene® 557ULX are versions of Kymene® 557H that contain low amounts of halide by-products.

Polyaminoamide/epichlorohydrin resins containing low amounts of halide by-products are disclosed in U.S. Patent No. 5,171,795, to Miller et al., European Patent Application Publication No. 0 488 767A2, to Bower, and European Patent Application Publication No. 0 510 987A1, to Bull et al.

Kymene® 450 wet strength resin is a polyaminoamide ureylene/epichlorohydrin resin prepared by reacting oxalic acid, methyl bis(aminopropylamine) and urea to form a polyaminoamide ureylene, which is then alkylated with epichlorohydrin. Resins of this type are disclosed in U.S. Patent No. 4,487,884, to Maslanka.

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Kymene® 736 is a polyalkylenepolyamine/epichlorohydrin resin prepared from hexamethylenediamine and epichlorohydrin as described in European Patent Application Publication No. 0508203, October 14, 1992.

5 The level of cationic polymer used will generally be in the range of from about 0.1 % to about 5 % on a dry basis based on the dry weight of pulp. A preferred level is from about 0.2 % to about 4 % , and a more preferred level from about 0.3 % to about 3 % . The most preferred level will be in the range of from about 0.3 % to about 2 % .

10 The aqueous pulp suspension of step (a) of the process of this invention is obtained by conventional means well known in the art, such as mechanical, chemical, semichemical, thermomechanical and chemi-thermomechanical pulping processes. After the mechanical grinding and/or chemical pulping step, the pulp is washed to remove residual pulping chemicals and solubilized wood components. Either bleached or unbleached pulp fiber may be utilized in the
15 process of this invention. Recycled pulp fibers are also suitable for use.

In step (b) of the process the cationic polymer and amphoteric polymer may be added to the pulp suspension separately in any order, or they may be mixed together and thus added to the pulp simultaneously. Generally, both the amphoteric polymer and the cationic polymer will be added as aqueous solutions.
20 However, in those cases where the materials are available neat, they may be added to the suspension in the neat form.

Step (c), sheeting and drying the pulp slurry, is carried out according to conventional means well known in the paper making art.

25 The paper of this invention has dry strength greater than that of paper that is the same except that it contains no amphoteric polymer. Conventionally used indicators of dry strength are tensile strength, Z-direction tensile strength (tensile

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strength in the thickness direction), Mullen burst strength and ring crush. The tensile strength of the paper of this invention is found to be from about 1 % to about 15 % greater, more particularly, from about 1 % to about 10 % greater, than that of paper that is the same except that it contains no amphoteric polymer.

5 Values of the tensile strength of the papers of this invention fall in the range of from about 4.5 to about 7.1 kg/cm width (25 to about 40 lb/inch width).

The process of this invention is of use in a large variety of paper types, e.g., liner board, liquid packaging board, corrugating medium, printing or writing paper, newsprint, and tissue or towel. It is of particular significance for

10 use in making liner board and corrugating medium from recycled pulp where chemicals often work poorly because of high levels of anionic materials present due to the recycling operations.

This invention is illustrated by the following examples, which are exemplary only and not intended to be limiting. All percentages, parts, etc., are

15 by weight, based on the weight of the dry pulp, unless otherwise indicated.

Examples 1-23

In these examples, which describe preparation of the amphoteric polymers of this invention, the equipment utilized was typically a two-liter resin kettle having a bottom valve with a stopcock. Fittings included a mechanical stirrer

20 (paddle), thermocouple, nitrogen sparge inlet, and a nitrogen outlet passing through an aqueous sodium metabisulfite trap. Initiator solutions were continuously injected into the reactor through hypodermic tubing using a syringe pump.

A solution of the monomers and copper sulfate in deionized water was

25 prepared, and the pH was adjusted to 4-5 using aqueous sodium hydroxide. The

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solution was transferred to a polymerization reactor, and then sparged with nitrogen to remove oxygen. A blanket of nitrogen was maintained on the reactants during polymerization. Polymerization was initiated by adding the redox initiator (potassium bromate/sodium metabisulfite) over a period of 30-60 minutes.

The following describes a typical preparation of an amphoteric polymer based on acrylamide, acrylic acid and MTMAC.

In a 600 ml beaker there were combined 300.00 g of distilled water, 2.87 g. acrylic acid, 8.28 g. 75% MTMAC solution, and 125.31 g. of aqueous acrylamide (52.6% solids, 23.2 ppm copper based on solids). Aqueous sodium hydroxide solution (1.21 g. of 50% solution) was used to adjust the pH to 4.5. Water was added (32.33 g.) to bring the total weight to 470 g. The resulting solution was transferred to the reactor and sparged with nitrogen at 6 SCFM while stirring for 45 minutes. The nitrogen sparge rate was then decreased to 2 SCFM. Fifteen milliliters each of 5 wt. % aqueous potassium bromate (1 weight percent based on total monomers) and 10 wt. % aqueous sodium metabisulfite (2 weight percent based on total monomers) were added to the reactor over 60 minutes at an addition rate of 15 ml per hour. The initial temperature was 24.4°C, and the maximum temperature reached after 25 minutes was 50.1°C. At the conclusion of the initiator addition, the reaction was stirred an additional fifteen minutes, and the thick reaction product was drained from the reactor and analyzed.

The polymer reduced specific viscosity (RSV) at 0.05% polymer concentration was measured by diluting 30.67 g. of a 1% aqueous solution of the reaction product to 50.00 g. with distilled water, and then to 107.1 g. with 19.6% aqueous sodium chloride solution. This provided a 0.05% polymer

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5 solution in 2 m sodium chloride solution. The flow time of the polymer solution in a Ubbelohde capillary viscometer at 30°C was 78.3 seconds compared to the flow time of 73.1 seconds for the 2 m sodium chloride control. The RSV was calculated using the following formula where 71.5 is the kinetic correction factor for the particular Ubbelohde viscometer. The RSV was calculated to be 1.46 dl/g. The Brookfield viscosity of the original 16.3% polymer solution was 3950 cps measured with a #4 spindle at 60 rpm and 25°C using a Brookfield LVT viscometer.

$$RSV = \frac{\frac{(t_s - \frac{71.5}{t_s})}{(t_o - \frac{71.5}{t_o})} - 1}{0.05}$$

Polymers made by this procedure are described in Table 1.

Table I
Amphoteric Acrylamide Polymers

| Example No. | Cationic Monomer (Mole.%) | Anionic Monomer (Mole.%) | MBA (Mole.%) | Copper Ion (ppm based on Acrylamide) | Polymerization Solids, % | KBrO ₃ /Na ₂ S ₂ O ₈ , % Based on Monomer | Initiator Addition Time, minutes | Final Solids, % | RSV (0.05%) dl/g |
|-------------|---------------------------|--------------------------|--------------|--------------------------------------|--------------------------|---|----------------------------------|-----------------|------------------|
| 1 | MTMAC(3) | AA (3) | -- | 25-30 | 15 | 1.33/1.67 | 40 | 15.8 | 1.16 |
| 2 | MTMAC(3) | AA (3) | -- | 25* | 15 | 1/2 | 60 | 15.8 | 2.17 |
| 3 | MTMAC(3) | AA (4) | -- | 25-30 | 15 | 1.33/1.67 | 40 | 15.8 | 1.1 |
| 4 | MTMAC(3) | AA (4) | -- | 23.2 | 15 | 1/2 | 60 | 16.3 | 1.46 |
| 5 | MTMAC(3) | AA (4) | -- | 30 | 17 | 1/2 | 50 | 18.5 | 1.11 |
| 6 | MTMAC(3) | AA (4) | 0.098 | 32 | 10 | 1/2 | 30 | 10.8 | 1.93 |
| 7 | MTMAC(3) | AA (5) | -- | 25-30 | 15 | 1.33/1.67 | 40 | 16.0 | 1.28 |
| 8 | MTMAC(3) | AA (5) | -- | 23.2 | 15 | 1/2 | 60 | 16.5 | 1.15 |
| 9 | MTMAC(3) | AA (5) | 0.033 | 25* | 15 | 1/2 | 60 | 20.8 | 1.48 |
| 10 | MTMAC(3) | IA (2) | -- | 27.8* | 25 | 1/2 | 60 | 22.6 | 1.46 |
| 11 | DMAEMA-HCl (3) | IA (2) | 0.098 | 25* | 15 | 1/2 | 60 | 16.2 | 1.49 |
| 12 | MTMAC(3) | MA (3) | 0.065 | 25 | 15 | 1/2 | 60 | 16.2 | 2.83 |
| 13 | MTMAC(3) | MA (4) | 0.065 | 25 | 15 | 1/2 | 60 | 16.5 | 1.34 |
| 14 | ATMAC (3) | AA (4) | -- | 25* | 15 | 1/2 | 60 | 16.8 | 2.01 |

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Table I, continued

| Example No. | Cationic Monomer (Mole %) | Anionic Monomer (Mole %) | MBA (Mole %) | Copper Ion (ppm based on Acrylamide) | Polymerization Solids, % | KBrO ₃ /Na ₂ S ₂ O ₈ , % Based on Monomer | Initiator Addition Time, minutes | Final Solids, % | RSV (0.05%) dl/g |
|-------------|---------------------------|--------------------------|--------------|--------------------------------------|--------------------------|---|----------------------------------|-----------------|------------------|
| 15 | ATMAC (3) | AA (5) | — | 25* | 15 | 1/2 | 60 | 16.0 | 1.87 |
| 16 | ATMAC (3) | IA (2) | — | 27.8* | 25 | 1/2 | 60 | 22.4 | 2.27 |
| 17 | ATMAC (3) | IA (2.5) | — | 23.2* | 20 | 1/2 | 60 | 23.1 | 1.32 |
| 18 | MBMAC(3) | AA (4) | — | 25.8 | 20 | 1/2 | 60 | 21.3 | 1.07 |
| 19 | MBMAC(3) | AA (4) | 0.049 | 25 | 15 | 1/2 | 60 | 16.8 | 2.33 |
| 20 | MBMAC(3) | AA (5) | — | 23.2 | 20 | 1/2 | 60 | 22.3 | 1.09 |
| 21 | MBMAC(3) | AA (5) | 0.049 | 25 | 15 | 1/2 | 60 | 16.7 | 1.88 |
| 22 | MBMAC(3) | IA (2) | 0.049 | 25* | 20 | 1/2 | 60 | 22.0 | 1.88 |
| 23 | MBMAC(3) | IA (2.5) | — | 23.2* | 20 | 1/2 | 60 | 21.9 | 1.09 |

* Versenex 80 added at 0.06% based on acrylamide for copper chelation.

All examples utilized acrylamide as the nonionic monomer

MTMAC = methacryloyloxyethyltrimethylammonium chloride

ATMAC = acryloyloxyethyltrimethylammonium chloride

DMAEMA-HCl = dimethylaminoethylmethacrylate hydrochloride salt

MBMAC = methacryloyloxyethylbenzyltrimethylammonium chloride

AA = acrylic acid

IA = itaconic acid

MA = methacrylic acid

MBA = methylenbisacrylamide

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For evaluation of the amphoteric polymers in paper, handsheets or paper from a continuous laboratory former were prepared. The Z-direction tensile strength, tensile strength, and ring crush was determined and compared with controls in which no amphoteric polymer was added. In all cases an additional cationic polymer, either cationic starch or Kymene®557H wet strength resin, an epichlorohydrin/polyaminoamide available from Hercules Incorporated, Wilmington, DE, were also incorporated.

Examples 24-32 and Comparative Example A

Several of the polymers made in Example 1-23 were tested as dry strength additives in paper handsheets prepared using 50:50 hardwood/softwood pulp at pH 7.0, to a nominal basis weight of 130 g/m² (80 lbs/ream). All paper included 0.4% Kymene 557® H wet strength resin and 0.225% Aquapel® 649 alkylketene dimer sizing agent (both available from Hercules Incorporated, Wilmington, DE), added in that order after the addition of 0.1-0.3% of the dry strength additives. The paper samples were aged under ambient conditions for at least two weeks before testing the tensile strength (TAPPI test method 541) and the tensile strength in the thickness direction (Z-Direction Tensile, TAPPI test method 494). The latter test is a good indicator of the strength of the internal bonding between paper fibers. The properties of samples containing dry strength additives was compared to those of the controls, which contained only the wet strength and sizing agents. The data are in Table 2. Comparisons in the table are calculated as percent improvements or:

$$\% \text{ Improvement} = [(\text{Strength with polymer}/\text{strength of control}) \times 100] - 100.$$

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The data in Table 2 demonstrate from about 2 to about 15% improvement in tensile strength for the papers of this invention as compared to paper with the same cationic polymer but no amphoteric polymer.

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Table 2
Evaluation of Handsheets Containing Amphoteric Acrylamide Polymers¹

| Example No. | Polymer ² | % Polymer | ZDT, lb/sq. in. | ZDT, % Improvement | Tensile, kg/cm width | Tensile, % Improvement |
|-------------|----------------------------|-----------|-----------------|--------------------|----------------------|------------------------|
| 5 24 | 3MTMAC/3AA (Example 1) | 0.1 | 62.85 | -8.5 | 6.52 | 2.5 |
| 25 | 3MTMAC/3AA (Example 1) | 0.2 | 73.9 | 7.6 | 6.91 | 8.5 |
| 26 | 3MTMAC/3AMA (Example 1) | 0.3 | 70.8 | 3.1 | 6.76 | 6.3 |
| 27 | 3MTMAC/4AA (Example 3) | 0.1 | 71.25 | 3.7 | 7.00 | 9.9 |
| 28 | 3MTMAC/4AA (Example 3) | 0.2 | 68.05 | -0.9 | 7.24 | 13.7 |
| 10 29 | 3MTMAC/4AA (Example 3) | 0.3 | 71.45 | 4.0 | 6.58 | 3.4 |
| 30 | 3MTMAC/5AA (Example 7) | 0.1 | 64.35 | -6.3 | 7.05 | 10.8 |
| 31 | 3MTMAC/5AA (Example 7) | 0.2 | 68.65 | -0.1 | 7.31 | 14.8 |
| 32 | 3MTMAC/5AA (Example 7) | 0.3 | 72.0 | 4.8 | 6.99 | 9.8 |
| A | None | -- | 68.7 | -- | 6.36 | -- |

15 1. All handsheets contain Kymene®557 wet strength resin and Aquapel®649 alkylketene dimer size at 0.4% and 0.225% respectively, based on the weight of the dry pulp used to prepare the handsheets.

2. MTMAC = methacryloyloxyethyltrimethylammonium chloride
 AA = acrylic acid

20 The polymers contain acrylamide and the indicated mole%'s of comonomer.

Examples 33-51 and Comparative Example B

Paper was made on a continuous laboratory former using mixtures of hardwood and softwood pulp. Paper testing was carried out as described for Examples 24-32 except that tensile strength was determined in both machine and cross direction and then averaged using the geometric mean of the machine and cross machine direction values. The results are presented in Table 3. The data in Table 3 demonstrate tensile strength improvements of up to about 9% for the papers of this invention as compared to paper with the same cationic polymer but no amphoteric polymer.

Examples 52-60 and Comparative Examples C-F

Paper was made on a continuous laboratory former using repulped old corrugated containers as pulp. Paper testing was carried out as described for Examples 24-32 except that tensile strength was determined in both machine direction and cross direction and then averaged using the geometric mean of the machine and cross machine direction values. In these examples cationic starch was utilized instead of Kymene 557® H wet strength resin. In some of the examples (so indicated) Aquapel® 649 alkylketene dimer sizing agent was replaced by rosin size plus alum. The results are presented in Table 4. The data in Table 4 demonstrate tensile strength improvements of up to about 7.5% for the papers of this invention as compared to paper with the same cationic polymer but no amphoteric polymer.

Table 3
Evaluation of Laboratory Former Paper
Containing Amphoteric Acrylamide Polymer¹

| Example No. | Polymer ² | % Polymer | ZDT, lb/sq. in. | ZDT, % Improvement | Tensile, ³ kg/cm width | Tensile, % Improvement |
|-------------|---|-----------|-----------------|--------------------|-----------------------------------|------------------------|
| 33 | 3MTMAC/3AA (Example 2) | 0.2 | 89.5 | -3.3 | 6.16 | -3.7 |
| 34 | 3MTMAC/3AA (Example 2) | 0.3 | 91.25 | -1.4 | 6.38 | -0.2 |
| 35 | 3MTMAC/4AA (Example 4) | 0.2 | 90.1 | -2.6 | 6.47 | 1.2 |
| 36 | 3MTMAC/4AA/ 0.098 MBA (Example 6) | 0.2 | 89.8 | -3.0 | 6.06 | -5.3 |
| 37 | 3MTMAC/4AA/ 0.098 MBA (Example 6) | 0.3 | 97.8 | 5.7 | 6.59 | 3.1 |
| 39 | 3MTMAC/5AA (Example 8) | 0.2 | 92.55 | -0.3 | 6.52 | 1.9 |
| 40 | 3MTMAC/5AA 0.033 MBA (Example 9) | 0.2 | 91.85 | -0.8 | 6.04 | -5.5 |
| 41 | 3MTMAC/5AA 0.033 MBA (Example 9) | 0.3 | 91.15 | -1.5 | 6.57 | 2.8 |
| 42 | 3MTMAC/2IA (Example 10) | 0.2 | 93.75 | 1.3 | 6.62 | 3.5 |
| 43 | 3MTMAC/3MA 0.065 MBA (Example 12) | 0.2 | 91.05 | -1.6 | 6.57 | 2.8 |
| 44 | 3MTMAC/4MA 0.065 MBA (Example 13) | 0.2 | 91.30 | -1.4 | 6.53 | 2.2 |

Table 3, continued

| Example No. | Polymer ² | % Polymer | ZDT, lb/sq. in. | ZDT, % Improve- ment | Tensile, ³ kg/cm width | Tensile, % Improve- ment |
|----------------|---|--------------|--------------------|----------------------------|---|-----------------------------------|
| 45 | 3MTMAC/4MA 0.065 MBA (Example 13) | 0.3 | 94.45 | 2.1 | 6.59 | 3.0 |
| 46 | 3ATMAC/4AA (Example 14) | 0.2 | 88.30 | -4.6 | 6.45 | 0.9 |
| 47 | 3ATMAC/4AA (Example 14) | 0.3 | 87.10 | -5.9 | 6.55 | 2.4 |
| 48 | 3ATMAC/5AA (Example 15) | 0.2 | 90.05 | -2.7 | 6.46 | 1.1 |
| 49 | 3ATMAC/2IA (Example 16) | 0.2 | 95.90 | 3.6 | 6.73 | 5.2 |
| 50 | 3ATMAC/2IA (Example 16) | 0.3 | 97.20 | 5.0 | 6.93 | 8.5 |
| 51 | 3ATMAC/2.5IA (Example 17) | 0.2 | 88.40 | -4.5 | 6.36 | -0.5 |
| B | None | — | 92.55 | — | 6.39 | — |

1. All handsheets contain Kymene®557 wet strength resin and Aquapel®649 alkylketene dimer size at 0.4% and 0.225% respectively, based on the weight of the dry pulp used to prepare the handsheets. The pulp used was a mixture of hardwood and softwood pulps.

2. MTMAC = methacryloyloxyethyltrimethylammonium chloride

AA = acrylic acid

IA = itaconic acid

MBA = methylenebisacrylamide

The polymers contain acrylamide and the indicated mole %'s of comonomer.

3. Tensile strength was determined in both the machine direction and the cross direction and then averaged using the geometric mean of the machine and cross direction value.

Table 4
Evaluation of Laboratory Former Paper
Containing Amphoterics Acrylamide Polymer¹

| Example No. | Polymer ² | % Polymer | % Cationic Starch | Size | % Size | % Alum | Tensile, ³ kg/cm width | Tensile, % Improvement |
|-------------|------------------------|-----------|-------------------|-------|--------|--------|-----------------------------------|------------------------|
| 52 | 3MTMAC/4AA (Example 5) | 0.15 | 0.75 | Rosin | 0.15 | 0.50 | 5.04 | 2.8 |
| 53 | 3MTMAC/4AA (Example 5) | 0.05 | 1.5 | Rosin | 0.15 | 0.50 | 5.07 | -0.5 |
| 54 | 3MTMAC/4AA (Example 5) | 0.15 | 1.5 | Rosin | 0.15 | 0.50 | 5.43 | 6.4 |
| C | None | — | 0.75 | Rosin | 0.15 | 0.50 | 4.90 | — |
| D | None | — | 1.5 | Rosin | 0.15 | 0.50 | 5.09 | — |
| 55 | 3MTMAC/4AA (Example 5) | 0.05 | 0.75 | AKD | 0.125 | — | 5.41 | 4.1 |
| 56 | 3MTMAC/4AA (Example 5) | 0.15 | 0.75 | AKD | 0.125 | — | 5.25 | 1.2 |
| 57 | 3MTMAC/4AA (Example 5) | 0.25 | 0.75 | AKD | 0.125 | — | 5.39 | 3.9 |
| 58 | 3MTMAC/4AA (Example 5) | 0.05 | 1.5 | AKD | 0.125 | — | 5.41 | 1.8 |
| 59 | 3MTMAC/4AA (Example 5) | 0.15 | 1.5 | AKD | 0.125 | — | 5.22 | -2.1 |

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Table 4, continued

| Example No. | Polymer ² | % Polymer | % Cationic Starch | Size | % Size | % Alum | Tensile, ³ kg/cm width | Tensile, % Improve- ment |
|----------------|---------------------------|--------------|-------------------------|------|-----------|-----------|---|--------------------------------|
| 60 | 3MTMAC/4AA (Example 5) | 0.25 | 1.5 | AKD | 0.125 | — | 5.72 | 7.3 |
| E | None | — | 0.75 | AKD | 0.125 | — | 5.20 | — |
| F | None | — | 1.5 | AKD | 0.125 | — | 5.32 | — |

1. The pulp used was repulped old corrugated containers.

2. MTMAC = methacryloyloxyethyltrimethylammonium chloride

AA = acrylic acid

The polymers contain acrylamide and the indicated mole %'s of comonomer.

3. Tensile strength was determined in both the machine direction and the cross direction and then averaged using the geometric mean of the machine and cross direction value.

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It is not intended that the examples presented here should be construed to limit the invention, but rather they are submitted to illustrate some of the specific embodiments of the invention. Various modifications and variations of the present invention can be made without departing from the scope of the appended claims.

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What is claimed is:

1. A process for making paper comprising:
 - a) providing an aqueous pulp slurry;
 - b) adding to the aqueous pulp slurry cationic polymer selected from the group consisting of cationic starch and cationic wet strength resin, and water-soluble amphoteric polymer made from monomers comprising: i) nonionic monomer selected from the group consisting of acrylamide and methacrylamide; ii) anionic monomer; iii) cationic monomer; and iv) crosslinking monomer comprising at least one water-soluble divinyl monomer.
2. The process of claim 1 wherein the amount of anionic monomer plus cationic monomer is less than 9 mole percent of the total of anionic, cationic and nonionic monomer in the amphoteric polymer.
3. The process of claim 1 wherein the anionic monomer is selected from the group consisting of α,β -unsaturated carboxylic acids and salts thereof.
4. The process of claim 1 wherein the anionic monomer comprises α,β -unsaturated carboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid and salts thereof.
5. The process of claim 1 wherein the cationic monomer is selected from the group consisting of methacryloyloxyethyltrimethylammonium chloride (MTMAC), acryloyloxyethyltrimethylammonium chloride (ATMAC),

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methacryloyloxyethylbenzyltrimethylammonium chloride (MBMAC),
dimethylaminoethylmethacrylate (DMAEMA) and salts of DMAEMA.

5 6. The process of claim 1 wherein the amount of anionic monomer plus
cationic monomer is less than 8 mole percent of the total of anionic, cationic and
nonionic monomer in the amphoteric polymer.

 7. The process of claim 1 wherein the amount of anionic monomer plus
cationic monomer is less than 7 mole percent of the total of anionic, cationic and
nonionic monomer in the amphoteric polymer.

10 8. The process of claim 1 wherein the water soluble divinyl monomer is
selected from the group consisting of N,N'-methylenebisacrylamide, ethyleneglycol
dimethacrylate and ethyleneglycol diacrylate.

 9. The process of claim 1 wherein the molar ratio of cationic monomer to
anionic monomer is from about 0.5:1 to about 2:1.

15 10. The process of claim 1 wherein the cationic polymer is wet strength resin
selected from the group consisting of polymeric amine/epihalohydrin resins, glyoxal
modified acrylamide copolymer resins, polyethyleneimines and polyvinylamines.

 11. The process of claim 1 wherein the cationic polymer is polymeric
amine/epihalohydrin wet strength resin selected from the group consisting of
20 polyaminoamide/epihalohydrin resins, polyalkylenepolyamine/epihalohydrin resins,

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aminopolymer/epihalohydrin resins, and polyaminoamide ureylene/epihalohydrin resins.

12. The process of claim 1 wherein the wet strength resin is polyaminoamide/epichlorohydrin resin produced by reacting adipic acid with diethylenetriamine to produce polyaminoamide that is then alkylated with epichlorohydrin

13. The process of claim 1 wherein the amphoteric polymer is added at a level of from about 0.05 % to about 4 % based on the dry weight of the pulp.

14. The process of claim 1 wherein the cationic polymer is added at a level of from about 0.1 % to about 5 % based on the dry weight of the pulp.

15. The process of claim 1 wherein the cationic polymer is cationic starch.

16. The process of claim 1 wherein the nonionic monomer is selected from the group consisting of acrylamide and methacrylamide, the cationic monomer is selected from the group consisting of methacryloyloxyethyltrimethylammonium chloride (MTMAC), acryloyloxyethyltrimethylammonium chloride (ATMAC), methacryloyloxyethylbenzyltrimethylammonium chloride (MBMAC), dimethylaminoethylmethacrylate (DMAEMA) and salts of DMAEMA; the anionic monomer is selected from the group consisting of α,β -unsaturated carboxylic acids and salts thereof; and the crosslinking monomer is selected from the group consisting of N,N'-methylenebisacrylamide, ethyleneglycol dimethacrylate and ethyleneglycol diacrylate; and

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wherein the molar ratio of cationic monomer to anionic monomer is from about 0.5:1 to about 2:1;

the cationic polymer is cationic wet strength resin which is the reaction product of epichlorohydrin with a polyaminoamide from adipic acid and diethylenetriamine, and
5 is used at a level of from about 0.1 to about 5% based on the dry weight of pulp; and

the amphoteric polymer is added at a level of from about 0.05 to about 4% based on the dry weight of pulp.

17. The process of claim 1 wherein the nonionic monomer is selected from the group consisting of acrylamide and methacrylamide; the cationic monomer is
10 selected from the group consisting of methacryloyloxyethyltrimethylammonium chloride (MTMAC), acryloyloxyethyltrimethylammonium chloride (ATMAC), methacryloyloxyethylbenzyltrimethylammonium chloride (MBMAC), dimethylaminoethylmethacrylate (DMAEMA) and salts of DMAEMA; the anionic monomer is selected from the group consisting of α,β -unsaturated carboxylic acids and
15 salts thereof; and the crosslinking monomer is selected from the group consisting of N,N'-methylenebisacrylamide, ethyleneglycol dimethacrylate and ethyleneglycol diacrylate; and

wherein the molar ratio of cationic monomer to anionic monomer is from about 0.5:1 to about 2:1;

20 the cationic polymer is cationic starch used at a level of from about 0.1 to about 5% based on the dry weight of pulp; and

the amphoteric polymer is added at a level of from about 0.05 to about 4% based on the dry weight of pulp.

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18. The process of any of the preceding claims further comprising sheeting and drying the pulp slurry to obtain paper.

19. Paper made by the process of claim 18.

20. The paper of claim 19 that has a dry tensile strength from about 1 % to about 15 % greater than that of paper that is the same except that it contains no amphoteric polymer.

21. Paper comprising cationic polymer selected from the group consisting of cationic starch and cationic wet strength resin, and water-soluble amphoteric polymer made from monomers comprising: i) nonionic monomer selected from the group consisting of acrylamide and methacrylamide; ii) anionic monomer; iii) cationic monomer; and iv) crosslinking monomer comprising at least one water-soluble divinyl monomer.

22. The paper of claim 21 wherein the amount of anionic monomer plus cationic monomer is less than 9 mole percent of the total of anionic, cationic and nonionic monomer in the amphoteric polymer.

23. The paper of claim 21 wherein the anionic monomer is selected from the group consisting of α,β -unsaturated carboxylic acids and salts thereof.

24. The paper of claim 21 wherein the anionic monomer comprises α,β -unsaturated carboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid and salts thereof.

25. The paper of claim 21 wherein the cationic monomer is selected from the group consisting of methacryloyloxyethyltrimethylammonium chloride (MTMAC), acryloyloxyethyltrimethylammonium chloride (ATMAC),
5 methacryloyloxyethylbenzyltrimethylammonium chloride (MBMAC), dimethylaminoethylmethacrylate (DMAEMA) and salts of DMAEMA,

26. The paper of claim 21 wherein the amount of anionic monomer plus cationic monomer is less than 8 mole percent of the total of anionic, cationic and nonionic monomer in the amphoteric polymer.

10 27. The paper of claim 21 wherein the amount of anionic monomer plus cationic monomer is less than 7 mole percent of the total of anionic, cationic and nonionic monomer in the amphoteric polymer.

15 28. The paper of claim 21 wherein the crosslinking monomer is selected from the group consisting of N,N'-methylenebisacrylamide, ethyleneglycol dimethacrylate and ethyleneglycol diacrylate.

29. The paper of claim 21 wherein the molar ratio of cationic monomer to anionic monomer is from about 0.5:1 to about 2:1.

20 30. The paper of claim 21 wherein the molar ratio of cationic monomer to anionic monomer is from about 0.6:1 to about 1.5:1.

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31. The paper of claim 21 containing amphoteric polymer at a level of from about 0.1 % to about 3 % based on the dry weight of the paper.

32. The paper of claim 21 containing cationic polymer at a level of from about 0.1 % to about 5 % based on the dry weight of the pulp.

5 33. The paper of claim 21 wherein the dry tensile strength is from about 1 % to about 15 % greater than that of paper that is the same except that it contains no amphoteric polymer.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/14010

| A. CLASSIFICATION OF SUBJECT MATTER | | |
|---|---|---|
| IPC(6) :D21H 17/38 US CL :162/168.3 According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
| Minimum documentation searched (classification system followed by classification symbols) U.S. : 162/168.3,164.1,164.3,164.6,168.2,175,183 | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | US 5,032,226 A (WINIKER ET AL) 16 JULY 1991, SEE ENTIRE DOCUMENT. | 1-33 |
| Y | US 2,884,058 A (SCHULLER ET AL) 28 APRIL 1959, SEE ENTIRE DOCUMENT. | 1-33 |
| Y | JP 5-51895 A (SEIKO KAGAKU KOGYO CO LTD) 02 MARCH 1993, SEE ENTIRE DOCUMENT. | 1-33 |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex. | | |
| * "A" | Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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| Date of the actual completion of the international search 23 OCTOBER 1997 | | Date of mailing of the international search report 24 NOV 1997 |
| Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230 | | Authorized officer PETER CHIN Telephone No. (703) 308-2046 |